



Reduction of NO with metal-doped carbon aerogels

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ABSTRACT

Copper- and cobalt-doped carbon aerogels, obtained from the polycondensation of resorcinol and formaldehyde, were used to study NO reduction. The interaction NO–carbon was studied under temperature programmed surface reaction (TPSR) conditions and by *in situ* FTIR adsorption of NO. Metal-doped carbons showed higher activity for NO conversion (about 80% at 450 °C) than free metal carbon. In this temperature range, the detected products are only N₂, CO and CO₂, but the conversion into N₂ is much lower than total NO conversion, meaning that some nitrogen compounds remain on the carbon surface. The metal species present in carbon aerogels participate both on the dissociation of NO and on the transfer of oxygen from the oxidized sites to the carbon matrix. The reaction mechanism depends on the temperature and contact time and involves the formation of surface complexes of type C(N), C(NO) and C(O₂). The decomposition of these complexes is favored by the presence of metal cations, leading to N₂, CO and CO₂ as final products which can be crucial for maintaining a high NO conversion rate. The reactions take place inside the micropores leading to the opening and creation of other pores. The best catalytic performance of copper-doped carbon aerogels is due to its ability to undergo redox cycles.

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1. Introduction

Nitrogen oxides (NO_x), among other atmospheric pollutants, are responsible for rain acidification and destruction of the stratospheric ozone layer, which justify the growing concern for reduction of NO_x from the exhaust of combustion sources. The potential application of carbon materials (chars, activated carbons) to exhaust purification has motivated the study of the NO_x–carbon reaction [1,2]. Activated carbon itself can reduce NO_x to N₂ without addition of an external reducing agent [2–4]. However, the reaction between NO and carbonaceous materials normally takes place at temperatures above 500 °C [5] being the catalytic behavior of carbon surface strongly dependent in their chemical and porous nature [6–8]. Important decreases on the temperature required for NO reduction can be observed when metal (alkali, alkaline-earth or some transition metals – Cr, Fe, Co, Ni and Cu) carbon supported catalysts are employed [9–12]. Illán-Gómez et al. [3,11] reported that during NO–carbon reaction, metal species participate in a redox mechanism, where the metal is oxidized by NO and reduced by carbon. As a consequence, the catalyst behavior is related with the initial state of metal before reaction (preferentially in a reduced state), its affinity towards NO and its redox properties. In fact,

carbon can be used both as a reducing agent and as a catalyst support. Metals are able to dissociatively chemisorb NO [11], but this compound can also be chemisorbed on the surface of the active carbon [13] and, as a result, surface oxides appear, while N₂ is released [14].

Carbon aerogels, prepared from the polymerization reaction of resorcinol–formaldehyde mixtures are new carbon materials with several advantages regarding classical activated carbons [15–19]. These materials have a great versatility as they can be tailored with controlled surface area and porosity and produced in different forms [17]. On the other hand, since carbon aerogels are synthesized from pure reagents, they are ash-free and pure carbon materials, thus avoiding the interference of any inorganic phase on the catalytic behavior of the carbon surface. Furthermore, conventional carbon materials contain inorganic compounds and nitrogen in its composition, which can difficult the evaluation of the origin of nitrogen that can be released from carbon surface during NO reduction [4]. Metal-doped carbon aerogels, which are susceptible to be used directly as catalysts, can be prepared by dissolving the corresponding metal precursor salt in the starting R–F aqueous solution [15,16]. Metals addition strongly influences the textural characteristics of the final carbon aerogel and results in homogeneous metal distribution in the carbon matrix, minimizing the metal sintering [18].

The aim of this work is to evaluate the different parameters that can determine the catalytic performance of metal-doped carbon

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aerogels in the catalytic reduction of NO to N₂. This is a first study, carried out in the absence of O₂ or additional reducing agent (hydrocarbons, NH₃), in order to be able to evaluate the interaction of NO with a pure carbon surface, the role of different transition metals (Co, Cu) and the influence of porosity. For that, many experimental techniques were used (mercury porosimetry and N₂ adsorption, TEM, DRX, TPSR, *in situ* FTIR) to analyze the evolution of the chemical and porous characteristics of the catalysts. Some mechanistic considerations have been suggested on the basis of the obtained results. The knowledge of these parameters will facilitate the design of more effective catalysts.

2. Experimental

2.1. Preparation and characterization of carbon aerogels

Carbon aerogels doped with metals were prepared according to a methodology presented in previous works [18,19]. The samples were obtained from sol–gel polymerization of resorcinol (R) and formaldehyde (F), using copper and cobalt acetates as precursor salts, leading to a final metal content of 3.4 and 4.2 wt.% in the carbon aerogel, respectively. Resorcinol and formaldehyde were dissolved in water (R/F molar ratio of 1:2). The metal acetate precursors were then dissolved in the same solution. Afterwards, the obtained solutions were cast into glass sealed molds and polymerized for 1 day at 25 °C, 1 day at 50 °C and 5 days at 80 °C. After the cure cycle, the gels were introduced into acetone during 48 h and then supercritically dried with carbon dioxide. The obtained organic aerogels were carbonized under N₂ flow up to 500 °C, with a heating rate of 1.5 °C min^{−1} and a soak time of 5 h. The samples will be referenced as AM-500, where M represents the metal and “500” indicates the carbonization temperature.

A carbon aerogel without metal was also prepared, in order to be used as reference. Na₂CO₃ was used as polymerization catalyst, with a molar ratio R/Na₂CO₃ of about 800, so Na amount can be neglected in the correspondent carbon aerogel.

The synthesized samples were characterized by N₂ adsorption (−196 °C), mercury porosimetry, X-ray diffraction, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM). Mercury porosimetry provides the particle density (ρ_p), the pore volume corresponding to pores with diameter between 3.7 and 50 nm, referred as “mesopore” volume (V_{meso}), the volume of pores with diameter greater than 50 nm, or “macropore” volume (V_{macro}) and the cumulative external surface area contained in the pores with a diameter greater than 3.7 nm (S_p). The experiments were carried out using the same equipments and conditions reported in previous works [18,19].

2.2. Temperature Programmed Surface Reaction (TPSR)

In order to study NO carbon interaction, TPSR experiments were carried out at atmospheric pressure, in a fixed bed reactor with 1.5 cm of diameter, using 300 mg of carbon aerogel (one run for ACu-500 carbon aerogel was performed using only 100 mg). The samples were previously milled to powder in order to have a continuous catalytic fixed bed. A reactant gas mixture containing 500 ppm of NO and He as balancing gas was supplied with a total

flow rate of 15 L h^{−1}, in a temperature range between 80 and 450 °C, with a heating rate of 5 °C min^{−1}.

Carbon aerogels were pre-treated in He at 120 °C during 1 h, before reaction. Some blank experiences were performed, subjecting the samples to an *in situ* heat treatment in He (15 L h^{−1}), with a heating rate of 5 °C min^{−1} in the temperature range between 80 and 450 °C.

The reactor outflow was analyzed simultaneously by an on-line gas chromatograph (5890 chromatograph HP Series II equipped with two columns, a Poraplot Q and 5A MolSieve, for N₂, O₂ and N₂O analysis), a chemiluminescence NO_x analyzer (Thermo Electron 42C NO–NO₂–NO_x high level), a mass spectrometer (Balzers, Prisma QMS200) and an IR analyzer for CO/CO₂ (Ultramat 23, Siemens).

2.3. Fourier Transformed Infrared Spectroscopy (FTIR)

The NO interaction with aerogels was analyzed by *in situ* FTIR experiments at different temperatures, under static conditions, in a closed cell. Wafers of about 10 mg cm^{−2}, prepared from a dilution (1:5 in weight) of the carbon aerogel in aerosil (A380) were pre-treated for 2 h at 120 °C, under dynamic vacuum (10^{−6} Torr).

The adsorption of NO was carried out at room temperature ($P_{\text{eq}} = 3.5$ Torr), followed by heating to 300, 400 and 500 °C, using a home built *in situ* transmission IR cell (quartz) equipped with CaF₂ windows. The spectra were recorded with a FTIR Thermo Nicolet Nexus (DTGS detector) spectrometer (64 accumulations for each spectrum with a resolution of 4 cm^{−1}).

3. Results and discussion

3.1. Catalysts characterization

The synthesis and characterization of metal-doped carbon aerogels have been described in previous works [18,19]. Table 1 summarizes the textural characteristics obtained for carbon aerogel samples. The structure of carbon aerogels consists in a three-dimensional network of overlapped nearly spherical particles, which can be observed in the TEM image of ACu-500 sample reported in Fig. 1(a).

The meso- and macropores correspond to the interparticle voids, and consequently their volume and size are controlled by the dimension of primary particles, while microporosity is mainly due to gases release during carbonization step. Thus, the microporosity and surface evolution will be described below. As previously commented, the particle size is strongly influenced by the presence of metals [15–19]. Therefore, samples A-500 and ACu-500, with smaller particles size, present similar textural properties characterized by the presence of mesopores (V_{meso} about 1 cm³ g^{−1}), large surface area of these pores (S_p between 100 and 200 m² g^{−1}) and S_{BET} of about 600 m² g^{−1}. In the case of ACu-500 sample, large particles size favors a macroporous system ($V_{\text{macro}} = 1.44$ cm³ g^{−1}) with a smaller S_{BET} surface area (<300 m² g^{−1}) because of the very small contribution of macropores to the surface values ($S_p = 2$ m² g^{−1}) in spite of the large macropore volume.

Table 1
Textural characteristics of carbon aerogels.

Sample	Metal content (wt. %)	ρ_p (g cm ^{−3})	V_{meso} (cm ³ g ^{−1})	V_{macro} (cm ³ g ^{−1})	S_p (m ² g ^{−1})	S_{BET} (m ² g ^{−1})
A-500	0.0	0.52	1.10	0.16	214	613
ACo-500	4.2	0.50	0.89	0.12	132	593
ACu-500	3.4	0.47	0.00	1.44	2	286

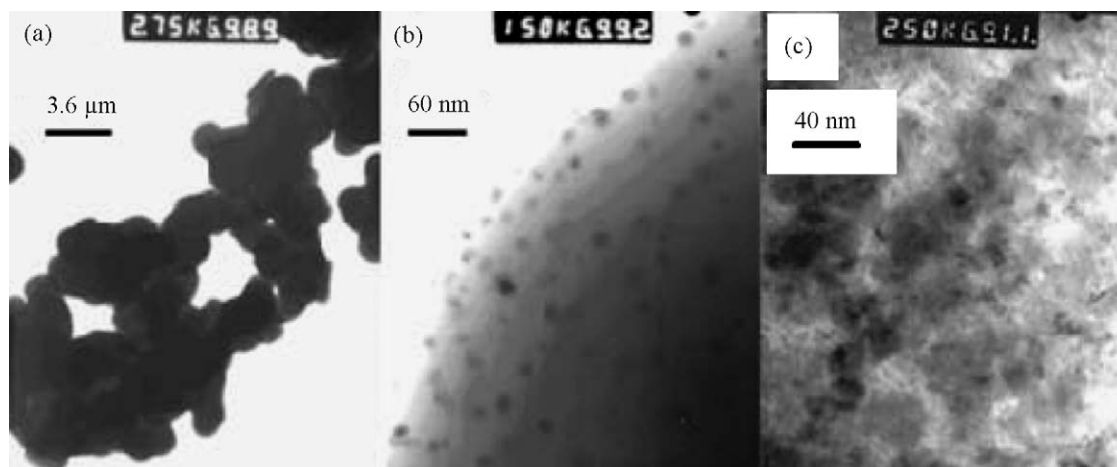


Fig. 1. High resolution transmission electron microscopy (HRTEM) image: morphology of ACu-500 catalyst (a), metal dispersion on ACu-500 (b) and ACo-500 (c).

As a consequence of the method used to incorporate metals into carbon aerogels, they seem to be well dispersed along the matrix, presenting a narrow distribution of metallic particles (nanometric scale), even after carbonization of the raw polymer. The HRTEM images of ACo-500 and ACu-500 samples are shown in Fig. 1(b) and (c). The best metal dispersion corresponds to ACo-500, where particles are difficult to detect even at high magnification. These results have been confirmed by XRD measurements since no peaks from extra metallic phase were detected.

The chemical structure of R-F polymer is composed by a network of R monomers linked between them by methyl or methylene ether bridges formed during the polymerization process. By carbonization, these bridges are progressively broken with increasing temperature, with the release of gases such as H₂O, CH₄, CO or CO₂ [20]. As the samples were obtained by carbonization at 500 °C under N₂ atmosphere, no further release of thermally unstable chemical groups was expected, below this temperature, during subsequent reactivity tests. Nevertheless, since after storage of samples, some of the oxygenated groups can be restored in the surface of carbons, TPD-experiments were carried out to evaluate the release of CO and CO₂, and these results will be used as blank experiments regarding the results obtained with NO.

The results reported in Fig. 2 for A-500, ACo-500 and ACu-500 samples show that significant amounts of CO₂ and CO are released below 450 °C in He flow. Release of CO₂ and particularly CO, is strongly favored by the presence of metals, being the nature and amount of surface groups, a function of the active metal incorporated in the carbon. It is well known [21] that the carbon materials heated under inert atmosphere release CO₂ molecules,

corresponding to the decomposition of carboxylic acid or lactones and CO molecules that can be associated to the decomposition of many groups such as phenol, ether, quinones or carbonyl groups, which are thermally more stable than those CO₂ evolving groups. In this case, the mesoporous materials (A-500 and ACo-500 samples) CO₂ release starts at lower temperature than with the ACu-500 sample. The CO₂ profiles of metal-doped carbon samples evidence a peak centered at about 270 and 350 °C for ACo-500 and ACu-500 samples, respectively. Thus, the release of CO₂ seems to be favored by large S_{ext} values and the presence of Cu induces the formation of more stable acid groups. At higher temperatures (420–440 °C), a very pronounced increase in the CO and CO₂ profiles can be observed, becoming impossible to distinguish the CO_x released due to the decomposition of either matrix polymer or surface oxygenated groups.

3.2. NO reduction: TPSR tests

The study of NO reduction was performed with samples pre-treated at 120 °C, whose surfaces are still saturated with carbon oxygen complexes. Therefore, during this study, the CO_x profiles previously referred will be taken into the account.

Fig. 3(a)–(c) shows the TPSR results obtained for the samples A-500, ACu-500 and ACo-500, respectively. The evolution of NO, N₂, CO and CO₂ are plotted as a function of temperature. For all samples, NO reduction is accompanied by CO and CO₂ formation, i.e. carbon gasification. Furthermore, N₂O or NO₂ were not detected as reaction products in all the temperature range.

The metal free carbon sample (A-500) shows the lowest NO conversion and the lowest N₂ amount formed at 450 °C. The NO

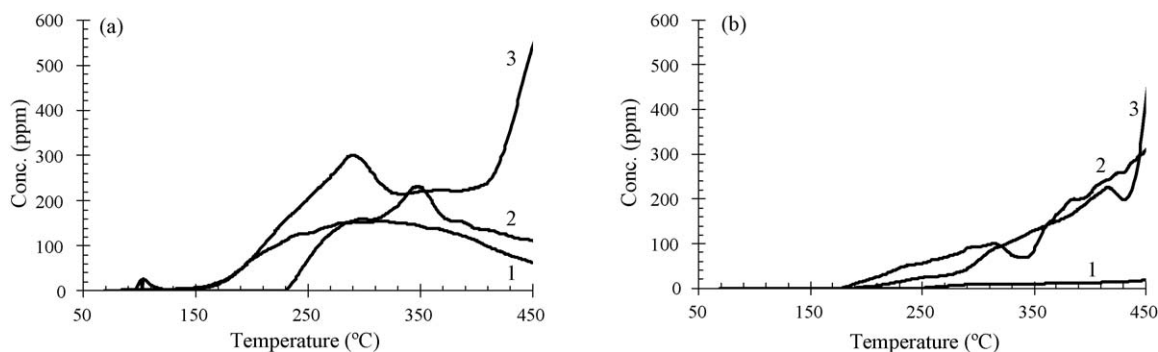


Fig. 2. Evolution of CO₂ (a) and CO (b) during heat treatment carried out (between 80 and 450 °C) under He flow on fresh samples A-500 (1), ACu-500 (2) and ACo-500 (3).

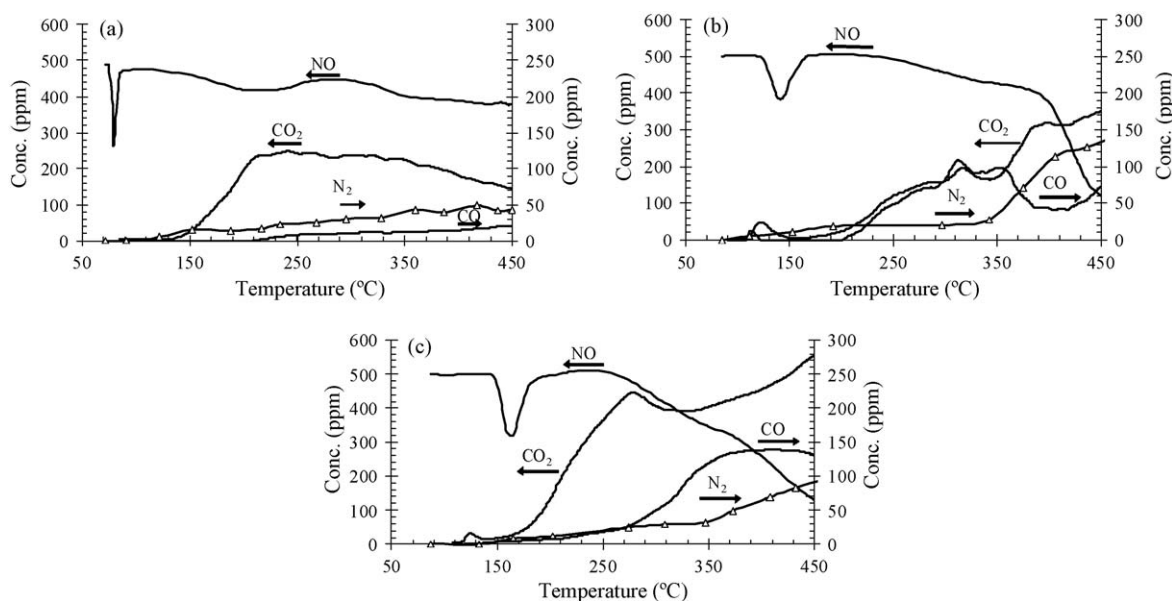


Fig. 3. Evolution of NO, N₂, CO e CO₂ concentrations, during TPSR measurements, for samples (a) A-500, (b) ACu-500 and (c) ACo-500.

profile shows, in this sample, a sharp decay at low temperature which is associated to a physisorption process on the carbon surface. With increasing temperature, physisorption is avoided while the reaction between both phases is favored. The formation of (CO₂ + N₂), as reaction products, begins at around 150 °C. The concentration of CO₂ presents a similar profile to that obtained in Fig. 2 (heating under He atmosphere), although showing an increase in concentration. The increase in CO₂ observed from 150 °C (about 240 ppm at 230 °C), coincides with a decrease in NO concentration and is accompanied by a slight release of nitrogen (about 25 ppm) in this temperature range. Taking into account that no other reaction products have been detected and being CO₂ the only carbon containing product, it seems that the reaction developed by NO on carbon surface can be globally described by:



However, the NO reduction and the CO₂ formation can also be developed on the existing oxygenated surface groups:



With increasing temperature, these surface groups were consumed and NO conversion decreases. At higher temperatures, the conversion increases again and, although CO₂ is still the main product, the product distribution changes: the CO₂ profile decays while CO presents the contrary behavior. The amount of N₂ that is released is lower than the expected by the analysis of NO concentration, i.e. some nitrogenated species remain bonded to the carbon surface.

The behavior of metal-doped carbon aerogel is significantly different, and is determined by the presence of metals. Thus, the NO profile presents in both cases a minimum at about 150 °C, due the enhanced chemisorption process induced from metal surfaces [3]. After surface saturation, the NO profile decay from 250 °C, more quickly in the case of ACo-500, but at 350 °C it presents a new inflection point, from which the slope of the curve is greater for ACu-500, in such a way that at 450 °C both catalysts present a similar NO conversion degree.

For ACu-500 sample, the concentration of N₂ is very low and nearly constant until 350 °C but it starts to increase significantly hereafter. Moreover, at the same temperature, the concentration of

CO₂ increases considerably while the concentration of CO begins to decrease. In the case of ACo-500 sample, the concentration of N₂ shows a first increase at about 200 °C (concomitant with a first increase in CO₂ release, when compared with A-500 sample) and a more significant one from approximately 350 °C. The analysis of CO₂ shows that the curve passes for a maximum (430 ppm) at approximately 280 °C, coincident with the position of the maximum (255 ppm) already seen in Fig. 2 (heating under He flow). Then, it decreases and remains constant between 310 and 350 °C. Moreover, an inflection in the curve of CO at the temperature of 310 °C can also be observed and, close to 350 °C, the concentration tends to stabilize while CO₂ concentration begins to rise again. Between 250 and 350 °C there is a decrease of about 150 ppm in NO concentration which is not accompanied by nitrogen evolution (about 30 ppm). As evidenced before for the other samples, it seems that nitrogenated species remain partially bonded to the carbon surface leading to a decrease in NO concentration in the reactor effluent, since no other nitrogen containing products can be detected. Oxygen atoms can be more easily released under the form of CO₂ or CO.

Comparing the evolution of CO for doped metal catalysts, obtained during heating with He (Fig. 2) and TPSR with NO diluted in He (Fig. 3), it appears that under inert gas the CO concentration always increases with the temperature, while during TPSR runs the CO concentration stabilizes (ACo-500) or begins to go down (ACu-500) from 350 °C. This tendency is also contrary to the observed on A-500 carbon sample.

The results presented in Fig. 3 show that, in all the cases, conversion of NO into N₂ is lower than the total conversion of NO. Table 2 presents the values of total NO conversion and conversion of NO into N₂, observed at 450 °C during TPSR measurements. NO conversion obtained with carbon without metal (A-500) is only 24%, while ACo-500 and ACu-500 samples present values of about 80%. The differences observed between total NO conversion and conversion into N₂ are significant, especially for metal-doped carbons that are much more active than carbon alone.

To compare the catalytic behavior, of A500 and ACu500 samples at similar values of NO conversion, the contact time (W catalyst (g)/F reactants (mol/h)) was reduced three times for ACu-500. In this test, the NO conversion at 450 °C ranged 30%, with practically total conversion into N₂. Under these experimental conditions, the

Table 2Total NO conversion and conversion of NO into N₂ at 450 °C.

Catalyst	Total NO conversion (%)	Conversion of NO into N ₂ (%)
A-500	24	18
ACo-500	79	38
ACu-500	80	56
ACu-500 (100 mg)	35	31

catalyst is totally selective into N₂, but when it is tested under conditions that lead to higher NO conversion, the catalyst is less selective for N₂. However, besides NO and N₂, it was not possible to detect other nitrogen compounds in the reactor effluent.

From mass spectrometry, the evolution of the signals $m/z = 32$ and $m/z = 46$, corresponding to O₂ and NO₂, respectively, have been monitored. No significant perturbation was observed during the TPSR measurements, in accordance with chemiluminescence and gas chromatography results, indicating that the oxygen resulting from NO decomposition totally remains in the carbon surface, generating oxygenated surface groups that are evolved mainly as CO₂ at higher temperature.

The signals $m/z = 27$ and $m/z = 42$, corresponding to the fragments –CN and –CNO/NCO, respectively, have also been monitored. These species were detected in some tests, as illustrated in Fig. 4 for A-500 sample, evidencing an increase in the signals intensity from 350 °C, in parallel with the increase in the formation of nitrogen and CO₂.

3.3. In situ FTIR adsorption of NO: interaction of NO with carbon surface species

The interaction of NO with the catalysts surface was studied by FTIR (Figs. 5–7). For simplicity, Figs. 5 and 6 only show spectra for ACo-500 sample because the corresponding spectra for other samples are similar to these ones. The spectra of studied materials initially present two main bands at 1437 and 1600 cm^{−1}, related to carbon support (Fig. 5). According to the literature, these bands are characteristic of C–H groups bending [22] and aromatic C=C groups stretching vibrations [23], respectively. Two others bands, less intense, can be observed at respectively 1660 and 1710 cm^{−1}, due to oxygenated surface groups. The band at 1660 cm^{−1} is assigned to quinone groups, while the band at 1710 cm^{−1} can be assigned to the C=O stretching vibration in carboxyl, ketone or aldehydes groups, in agreement with results showed in Fig. 2.

Independently of the sample, FTIR spectra practically do not change after NO introduction, at room temperature, suggesting a very weak interaction of NO with the carbon surface, as reported by Zawadzki and Wisniewski [23]. However, with increasing temperature, the formation of new bands in the regions 1700–1900 and 1400–1690 cm^{−1}, is observed (see difference spectra shown in Fig. 6), pointing out that the interaction of NO with the carbon

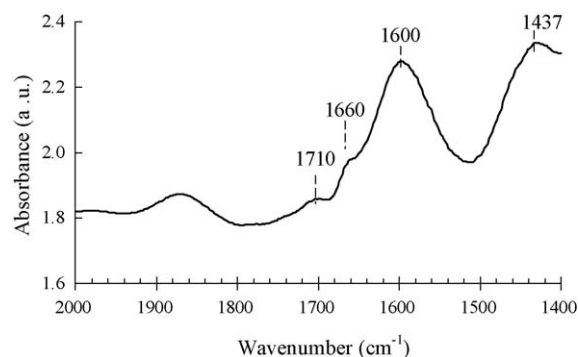


Fig. 5. FTIR spectra obtained for sample Co-500 after pre-treatment, before contact with NO at room temperature.

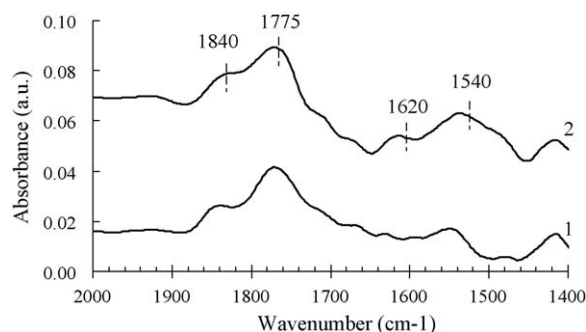


Fig. 6. FTIR spectra obtained for sample Co-500 after contact with NO at 200 °C (1) and 300 °C (2) during 1 h.

surface generates different types of surface groups. Bands around 1775 and 1840 cm^{−1} are probably due to lactones and anhydride groups [23]. A broad band centered at 1540–1550 cm^{−1} can be ascribed to the asymmetric stretching vibration of organic

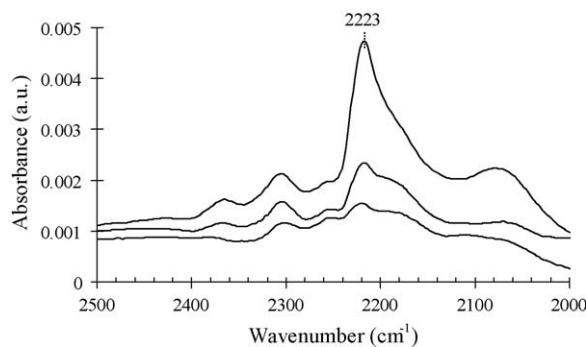


Fig. 7. FTIR spectra obtained for sample A-500 after contact with NO during 1 h at (1) 300 °C, (2) 400 °C and (3) 500 °C.

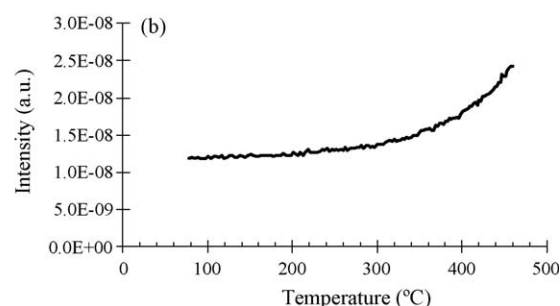
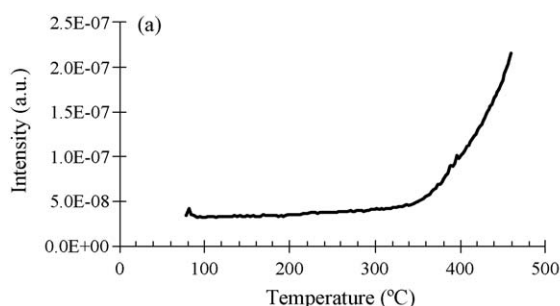


Fig. 4. Evolution of fragments $m/z = 27$ (a) and $m/z = 42$ (b) observed during TPSR measurements for the sample A-500.

nitrocompounds (R–NO₂) [23,25]. Heating at 300 °C, a new band, assigned to asymmetric stretching vibrations of nitrocompounds in extended aromatic system, appears at 1490 cm⁻¹ [23]. Bands in the range 1600–1690 cm⁻¹ are probably due to nitritocompounds (R–O–NO) [25]. The band at 1710 cm⁻¹ is due to surface carbonyl groups [24]. For higher temperatures (400, 500 °C), a new band at around 2220 cm⁻¹ is observed from difference spectra (Fig. 7) for the sole metal-free carbon sample which has been attributed to –CN and/or –NCO nitrogen groups.

3.4. Evolution of the catalyst characteristics after NO interaction

According to previously exposed results, NO reduction and carbon surface gasification as CO or CO₂ are simultaneous processes. As a consequence, the porous texture of the catalyst is progressively changing with the reaction development. This aspect was studied by analyzing the corresponding nitrogen adsorption isotherms of fresh and used catalysts. The *t*-plot method was used to determine (Table 3) micropore volume (*W*₀), surface of micropores (*S*_{mic}) and the external surface area (*S*_{ext}) of meso and macropores.

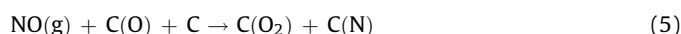
The results obtained are in good agreement with those obtained by mercury porosimetry, previously discussed (Table 1). Thus, fresh A500 and ACo-500 samples present higher surface area values as a consequence of the mesopores contribution. This is pointed out by the high values of the *S*_{ext}. It is noteworthy that in all the cases *S*_p < *S*_{ext} because mercury porosimetry cannot take into account the complete mesoporosity. However, the surface of ACu500 corresponds to the micropore surface, as macropore contribution (*S*_{ext}) is too small. The micropore surface is, in all the cases, of about 300 m² g⁻¹. It is observed that all the used catalysts present higher surface area than the fresh ones, due the development of the microporosity. The carbon gasification produces a pore opening, leading to a microporosity increase and also an enlargement of mesopores into macropores. As a consequence, a decrease in *S*_{ext} in the mesoporous catalysts (mainly in A500 sample) was observed, while in the case of ACu-500 sample, the transformation of some micropores into mesopores, lead to an increase in *S*_{ext}. This means that there are no diffusion limitations and that reaction takes place mainly inside the carbon microporosity and the behavior of the different catalysts is therefore only a function of the ability of metals to develop the NO reduction reaction.

A catalysts gasification degree of about 30% was observed, but XRD analysis of the used catalysts do not present any diffraction peak corresponding to the metallic phase. This means that the structure of carbon aerogels is able to avoid metal sintering, even under these experimental conditions, which is a guarantee of catalyst stability if additional reducing agents are fed.

3.5. Mechanistic considerations

Various forms of NO interaction with carbonaceous compounds have been suggested [5,8,24,26] resulting in mechanistic hypoth-

esis that justify the formation of N₂, CO and CO₂. The mechanism of N₂ formation is not yet well defined, although some authors defend that it depends on the temperature and the type of carbon matrix [5,26,27]. The results previously exposed, clearly pointed out that this reaction develops through the formation of oxygenated and nitrogenated intermediate species, which are responsible for the observed unbalances. The formation of surface C(N) and C(NO) complexes at temperatures between 200 and 300 °C confirms these observations. Eqs. (3)–(5) describe the formation of these intermediates [3,5]:



The NO chemisorption is enhanced by the presence of transition metals relatively to the carbon surface. The NO chemisorption on transition metals is dissociative and the atomic O or N species are progressively transferred to the carbon surface with increasing temperature. Therefore, the extent of these processes depends on the metal activity and the characteristics of the carbon surface. The surface complexes that are formed can occupy all active sites at the carbon surface, leading to the surface saturation [5], which can explain the decrease in NO concentration observed at temperatures lower than 350 °C, when no significant amounts of N₂ are detected. In our case, ACo-500 sample shows a higher activity in this temperature range, because it presents better metal dispersion (Fig. 1) and larger surface area (Tables 1 and 3) than ACu-500.

The nitrogenated complexes C(N) and C(NO) are quite stable [5,23] in comparison with the oxygenated ones. At low temperatures mainly C(O₂) species are evolved as CO₂. The decomposition of C(N) and C(NO) is an activated process [5], that occurs at higher temperatures and can be the rate-determining step of the reaction. In Fig. 3(b) and (c), for metal-doped carbon aerogels, a rapid increase in the N₂ formation at about 350 °C was shown, meaning that decomposition of complexes C(N) and C(NO) catalyzed by metals begins approximately at this temperature. The metals participate both on the chemisorption/dissociation of NO and on the transfer of species to the carbon surface, undergoing consecutive oxidation–reduction cycles by NO and carbon surface species, respectively. ACu-500 is more active than ACo-500 for this process, because the reduction of the oxidized metallic species (Cu–O_x vs Co–O_x) by carbon is straightforward in this reaction temperature range. This seems to be the limiting step in the NO reduction reaction. The ability of each metal to develop oxidation–reduction cycles determine the different N₂ conversion values (Table 2).

Taking into account the evolution of the product distribution and the low thermal stability of the CO₂-evolving groups, Eqs. (5) and (6)–(10) can explain N₂ formation and the increasing of CO₂ concentration while CO concentration becomes constant (Fig. 3) or begins to decrease, in metal-doped samples:

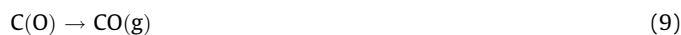


Table 3
Evolution of the catalysts surface characteristics.

Sample	<i>S</i> _{BET} (m ² g ⁻¹)	<i>t</i> -plot analysis		
		<i>W</i> ₀ (cm ³ g ⁻¹)	<i>S</i> _{mic} (m ² g ⁻¹)	<i>S</i> _{ext} (m ² g ⁻¹)
A500-fresh	613	0.13	296	317
A500-used	811	0.24	586	225
ACo500-fresh	593	0.16	353	240
ACo500-used	670	0.20	447	223
ACu500-fresh	286	0.08	291	5
ACu500-used	437	0.16	375	62

Results obtained by N₂ adsorption at –196 °C. *S*_{BET} = BET surface area, *W*₀ = micropore volume, *S*_{mic} = micropore surface, *S*_{ext} = external surface area.

According to Eqs. (5), (6) and (10) the CO₂ formed at higher temperatures comprises either the consumption of C(O) groups or gaseous CO and C(O₂) groups. Reactions (7) and (8) can also explain the increase in NO conversion into N₂ observed at high temperature (>350 °C) mainly for metal-doped carbons that have higher activity for decomposition of C(N) complexes.

Therefore, the catalytic behavior depends on the surface equilibrium between the different intermediates. It is noteworthy that at low contact times (see test performed with 100 mg ACu-500) the catalysts are highly selective, i.e. NO is totally transformed in N₂ (Table 2). However, increasing the amount of catalyst the NO conversion increases, but the N₂ formation does not increase in the same proportion. According to the sequential reaction mechanism previously discussed, in a first stage the NO chemisorption (reaction (3)) and dissociation (reaction (4)) lead to a high coverage of intermediate surface complexes, from which C(O₂) groups are quickly evolved, remaining the C(O) and C(N) ones. In the second step, because carbon surface is really covered, reaction mainly develops by oxidation of C(O) groups to C(O₂) by additional NO molecules (reaction (5)), which simultaneously increase the surface concentration of C(N) surface groups. The formation of N₂ is progressively favored by this process because it is formed from two adjacent C(N) groups (reaction (7)) or by reaction of these groups with additional NO molecules (reaction (8)). This means that the N₂ formation strongly depends on the available NO concentration.

In the absence of metals, NO chemisorption takes place directly on carbon surface and its reduction occurs based on similar mechanistic approaches, but the rate of dissociation and transfer of species is, in this case, lower than in the presence of metals. Moreover, the decomposition of surface C(N) complexes is probably extremely slow in all temperature range (from 150 to 450 °C) and reactions (7) and (8) do not occur in a great extension. It is important to remember that FTIR spectra (Fig. 7) well evidence the existence of several C(N) complexes that present a significant stability even at 500 °C, meaning that they have a longer half-life at lower temperature than when they are formed on the surface of metal-doped carbons. Moreover, elemental chemical analysis performed on used catalysts in NO TPSR tests confirmed the existence of nitrogen that in the case of sample A-500 reach a content of 0.35 wt.% in nitrogen. In the case of the used metal-doped carbon samples the nitrogen content was below the detection limit of the analysis.

4. Conclusions

The obtained results show that the carbon aerogels doped with transition metals are very active in NO reduction, in absence of oxygen. The high activity and selectivity of Cu-doped catalyst for reduction of NO into N₂ is related to its capacity for undergoing progressive cycles of oxidation by NO and reduction by the carbon matrix. Carbon surface also presents itself some catalytic activity, though with a low conversion in N₂. The reaction mechanism depends on the temperature and involves the formation of surface complexes of the type C(N), C(NO) and C(O₂). The decomposition of

these complexes is activated by metals supported in the carbon, leading to N₂, CO and CO₂ as final products.

From these results it can be emphasized that the presence of metal has an important role in the reaction mechanism of formation/decomposition of intermediary complexes that lead to N₂. The NO reduction and the carbon matrix gasification occur simultaneously because carbon is the unique reducing agent present in the system. The porous texture of catalyst does not present diffusion problems and the NO reduction takes place inside the micropores leading to the opening and creation of other pores. Future works will be carried out using an external reducing agent (NH₃ or hydrocarbons).

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